REMARKS

Favorable reconsideration of this application is requested in view of the following remarks.

Claim 23 has been amended editorially.

Claims 23-31 have been rejected under 35 U.S.C. 103(a) as being unpatentable over Shiraishi et al. (U.S. Patent No. 6,989,289) in view of Schmidt (U.S. Patent Application Publication No. 2004/0054041). Applicants respectfully traverse this rejection.

Claim 23 is directed to a capacitor and recites that the capacitor includes a positive electrode of a valve metal, a dielectric of an anodized film formed on the valve metal, and a negative electrode including a composite material in contact with the anodized film. Claim 23 further recites that the composite material of the negative electrode includes a conductive polymer and an ionic liquid that can repair a defect in the anodized film.

This rejection relies on Schmidt's disclosure of the ionic liquid by citing the portions of Schmidt referring to Mori et al. (JP 10-265674) and Fuller et al. (Molten Salt Forum (1998), 5-6 (Molten Salt Chemistry and Technology 5), 605 attached hereto) in the "Prior art" section (see page 3 of the July 8, 2010 Office Action and paras. [0013]-[0014] of Schmidt). Schmidt is directed to a mixture of polymers and ionic liquids for binder and adhesives and does not disclose the ionic liquids to be used in a capacitor or for a similar purpose. Thus, Schmidt is not an analogous art to claim 1 of the present application. The rejection also does not cite the other portions of Schmidt.

Even if Mori and Fuller et al. were considered as the references for the rejection instead of Schmidt, there is no reasonable basis to combine the conductive polymer disclosed in Shiraishi with the ionic liquid disclosed in Mori or Fuller as claim 23 recites.

Mori discloses a mixture of a non-conductive solid polymer and an ionic liquid (see para. [0008]) and further discloses that the conductive polymer could not provide sufficient physical strength because the ion conductivity would be derived from thermal

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agitation of the polymer, which reduces the physical strength of the polymer (see paras. [0004]-[0005]). Thus, Mori teaches away from a combination of a conductive polymer and ionic liquid for a composite material in a capacitor, as claim 23 recites.

Fuller discloses an ionic liquid-polymer gel composite and states that the composite has properties such as high conductivity, dimensional stability, etc. suitable for batteries, fuel cells, or capacitors (see abstract). Fuller also discloses that the ionic conductivity of the composite such as ionic liquid-PVdF(HFP) gel and salt-aPEO (amorphous polyethylene oxide) gel decreases when the mass ratio of the non-conductive polymer relative to the ionic material increases (see tables 1 and 2 on pages 606 and 608, respectively, and Fig. 1 on page 607). The properties of the non-conductive polymers of Fuller would be different from those of conductive polymers, which generally increase conductivity when the amount in a product increases. In addition, the other properties of the non-conductive polymer of Mori or Fuller, for example the physical strength, which would affect the dimensional stability sought by Fuller, would be different from those of the conductive polymers (see paras. [0004]-[0005] of Mori).

Further, Fuller discloses that the ionic conductivity of the ionic liquid-PVdF(HFP) gel increases when temperature increases from the room temperature (23 °C) to 100 °C (see Fig. 1). There is no reasonable basis to assume that those of skill working on a capacitor would use for a capacitor the ionic liquid of Fuller when the stable conductivity of the capacitor in a wide range of temperature and sufficient conductivity at the room temperature would not be expected from use of the ionic liquid of Fuller (see Fig. 1).

Accordingly, in total, there is no reasonable basis to combine the ionic liquid disclosed in Mori or Fuller with the conductive polymer of Shiraishi. Claim 23 and claims 24-31, which ultimately depend from claim 23, are thus distinguished from Shiraishi in view of Mori and Fuller disclosed in Schmidt.

Claim 32 is directed to a method of improving a withstand voltage of a capacitor and recites that a negative electrode including a composite material that contains a conductive polymer and an ionic liquid, similar to claim 23. Thus, for at least the same reasons as discussed for claim 23 above, claim 32 is distinguished from Shiraishi in view of Mori and Fuller disclosed in Schmidt. Accordingly, this rejection should be withdrawn.

In view of the above, Applicants request reconsideration of the application in the form of a Notice of Allowance.
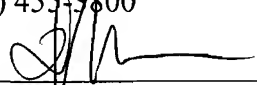
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Dated: October 8, 2010

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DPM/my/jes

Ionic Liquid-Polymer Gel Composite Electrolytes

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Abstract

We have performed preliminary studies examining the electrochemical properties of new electrolytes produced by mixing room-temperature ionic liquids or other imidazolium salts with the organic polymers. These salt-and-polymer blends exhibit exceptional properties, i.e. high conductivity, thermal stability, nonvolatility, and dimensional stability, for application in batteries, fuel cells, or capacitors as highly conductive polymer electrolytes.

Introduction

Ion conductive macromolecular gels and membranes have received much attention due, in part, to their potential promise as electrolytes in rechargeable lithium cells. We have extended our work in the area of room-temperature ionic liquids to explore molten salt polymer blends as gel electrolytes. Recently we described the first preparation and properties of novel ionic liquid-polymer gel electrolytes that are freestanding, flexible films composed of an air-stable, room-temperature perfluoroanion ionic liquid and poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF(HFP)).[1] Because these materials contain a pure salt (i.e., the ionic liquid component) supported within a polymer matrix, they bear similarities to the ionic rubber electrolytes being developed by C. A. Angell and coworkers. [2] In addition to these free standing gels, we will describe in this paper the preparation and properties of gels composed of amorphous poly(ethylene oxide) (aPEO) and 1-ethyl-3-methylimidazolium hexafluorophosphate (EMIPF$_6$).

The perfluoroanion ionic liquids used to prepare the ionic liquid-polymer gels have a number of beneficial properties: (*i*) high ionic conductivities; (*ii*) wide electrochemical windows; (*iii*) negligible volatility; (*iv*) nonflammability; (*v*) high thermal stability; and (*v*) subambient temperature operation. [3-7] Because of these characteristics, the neat perfluoroanion ionic liquids are promising candidates as electrolytes for batteries, [5,7-9] (including lithium and lithium-aluminum anode systems [7-9]), photovoltaic devices, [10] and capacitors [11] and as solvent media for homogenous catalysis. [12] Importantly, the ionic liquid-polymer gels offer the same benefits and potential applications as the neat ionic liquids but in a solid-state electrolyte.

Experimental

Ionic liquid-PVdF(HFP) gels were prepared as described in earlier publications. [1] This procedure entails mixing appropriate quantities of the ionic liquid and PVdF(HFP) powder with either 4-methyl-2-pentanone (MP) or propylene carbonate (PC) organic solvents, gelling the resulting mixture at *ca.* 75 °C in an aluminum pan, and finally removing the organic solvent by heating under vacuum for PC or by evaporation in air for MP. The resulting gel was a free-standing, rubbery film (thickness ≈ 0.05 cm; area = 20 cm^2) and was transparent to slightly translucent in appearance.

The aPEO gels were prepared by combining the 4 g of aPEO and 4 g EMIPF$_6$ and heating at 80 °C for 1 week. The EMIPF$_6$ salt dissolved completely into the polymer in a matter of hours;

however, the gel was left in the oven to ensure complete mixing of the polymer and salt. The resulting polymer-salt composite was a colorless, highly viscous gel.

Ionic conductivities were determined from electrochemical impedance spectroscopy (EIS) using the high frequency real axis touchdown of the Nyquist plots. Measurements were made on disks cut from the parent gel electrolyte film and having known areas of 0.19 to 0.55 cm^2. The conductivity cell was a PFA Swagelok® union tee fitted with a Teflon® spacer ring and two 1/2" diameter stainless steel rods to serve as the contact electrodes. [1] For elevated temperature studies, the "tee-cell" was wrapped with heating tape, and the temperature was regulated with a digital temperature controller. Staircase cyclic voltammograms were performed at a 33 µm glassy carbon electrode (Bioanalytical Systems, Inc.) with a platinum wire quasi-reference electrode and an aluminum wire counter electrode. The experiments were recorded with an EG&G Princeton Applied Research Model 273a potentiostat/galvanostat controlled with the PAR Model 270 software package. AC impedance spectra were recorded using an EG&G Model 263 potentiostat and lock-in amplifier controlled by the PAR Model 398 software in a frequency range of 10 Hz to 100 KHz.

Results And Discussion

Ionic conductivities of ionic liquid-PVdF(HFP) gel electrolytes. The ionic conductivities (κ) of ionic liquid-PVdF(HFP) gels made with $EMIBF_4$, EMI(triflate), and $EMIPF_6$ were investigated as functions of ionic liquid:PVdF(HFP) mass ratio and of temperature. Conductivities at room temperature (22 - 23 °C) and 100 °C on each gel are collected in Table 1. The logarithmic plots of ionic conductivity versus T^{-1} for the gels and the corresponding neat ionic liquids approximated simple Arrhenius behavior (*i.e.*, $\kappa = exp(-E_a/RT)$) over the limited temperature range examined in these studies. Least squares fits of the simple Arrhenius equation to the $EMIBF_4$-PVdF(HFP) and EMI(triflate)-PVdF(HFP) gel conductivity data are shown in Fig. 1. Although not apparent in the data given here, deviation from Arrhenius behavior is expected for data collected over a wider temperature range, [2,3] especially at subambient temperatures near the melting points of the neat ionic liquids (m.p. $EMIBF_4$ = 12 - 12.5 °C [7]; m.p. EMI(triflate) = -9 °C [6]). The room-temperature ionic conductivity of a transparent 1:1 $EMIPF_6$-PVdF(HFP) gel remained constant at 6.0 (±0.5) mS cm^{-1} after being under vacuum for 40 min at 60-70 °C. With continued vacuum heating, the conductivity gradually decreased to 2.0 mS cm^{-1} (120 min), and the gel developed a translucent foggy appearance as the $EMIPF_6$ crystallized. Continued solvent removal (273 min) produced an opaque white sample with a conductivity <0.01 mS cm^{-1}. A sample of the opaque white 1:1 $EMIPF_6$-PVdF(HFP) gel (273 min) was subjected to a temperature dependent conductivity study. Upon heating to 40 °C, the conductivity rose from <0.01 mS to 0.24 mS cm^{-1}. Continued temperature increases produced conductivities of 0.62 and 1.2 mS cm^{-1} at 60 and 80 °C, respectively.

Table 1. Ionic conductivity parameters for IL-PVdF(HFP) gel electrolytes and neat ionic liquids.

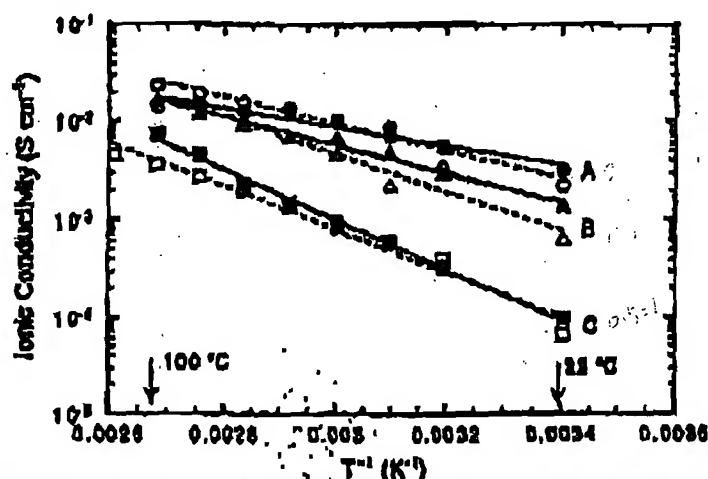| Ionic Liquid	Mass Ratio	κ/mS cm^{-1} 22-23°C	κ/mS cm^{-1} 100 °C	E_a/kcal mol^{-1}
EMI(triflate)	2:1 (MP)	2.2	22.9	6.6
EMI(triflate)	1:1 (MP)	0.6	9.1	8.0
EMI(triflate)	0.4:1 (MP)	0.06	4.5	8.5
$EMIBF_4$	2:1 (PC)	3.2	14.4	5.0
$EMIBF_4$	1:1 (PC)	1.4	16.4	6.6
$EMIBF_4$	0.5:1 (PC)	0.1	7.3	11.7
EMI(triflate)	neat	9.3	55.3	4.2
$EMIBF_4$	neat	13.8	59.0	4.3

Fig. 1. Ionic Conductivities of EMIBF$_4$-PVdF(HFP) (solid symbols) and EMI(triflate) (open symbols) gel electrolytes. Ionic liquid:PVdF mass ratio: (A) 2:1; (B) 1:1; (C) 0.5:1 for EMIBF$_4$ and 0.4:1 for EMI(triflate).

From Table 1 and Fig. 1, several observations can be made: (1) The ionic conductivities of the gels increase as the ionic liquid:PVdF(HFP) mass ratio increases. This also tracks with the physical characteristics of the gels, which progress from a relatively stiff film at the 0.4:1 or 0.5:1 mass ratio to a flexible film at the 2:1 weight ratio. (2) The E_A values increase with decreasing ionic liquid:PVdF(HFP) mass ratios so that the enhancements in κ with increasing mass ratios are not as dramatic at 100 °C as they are at room temperature. In fact, at 100 °C, κ for 1:1 EMIBF$_4$-PVdF(HFP) is actually greater than κ for 2:1 EMIBF$_4$-PVdF(HFP), though subtle differences in sample preparation may be partially responsible for this inversion in expected conductivities. The effects of E_A on the gel ionic conductivites are most clearly seen in Fig. 1. (3) The ionic conductivities of the gels track with the ionic conductivities of the corresponding neat ionic liquids. Therefore, neat EMI(triflate) and EMIBF$_4$ possess similar ionic conductivites as do their gels.

We have also demonstrated that the ionic liquid-PVdF(HFP) gel electrolytes can be operated at temperatures in excess of 200 °C and have found the conductivity of a 1:1 EMI(triflate)·PVdF(HFP) gel to be 41 mS cm^{-1} at 205 °C.[1] Subambient investigations of the physical properties of these gels are currently underway.

Properties of aPEO-based electrolytes Presented in Table 2 are the conductivities of several aPEO blends using various salts. Addition of the salt to the polymer increases the ionic conductivity of the polymer, yet the polymer does not dramatically decrease the conductivity of salt, when the salt is a room-temperature ionic liquid. More importantly, the salt-and-polymer blended systems allow higher melting salts to function as polymer electrolytes at room-temperature. An example of this is shown in Figure 2 by the cyclic voltammogram of 1:1 aPEO:EMIPF$_6$ gel which displays an electrochemical window of approximately 4.5 V. The window is defined by the reduction of the EMI$^+$ cation and the oxidation of the PF$_6^-$ anion and is typical of room-temperature ionic liquids (e.g. EMIBF$_4$).

Table 2. Conductivity data for salt-and-polymer blends using aPEO as the polymer component.

Salt-and-Polymer	Melting Point of Pure Salt(°C)	Conductivity (mS cm^{-1})
aPEO only	—	9.3×10^{-6}
1:1 EMIPF$_6$:aPEO	58 - 60	0.61
2.8:1 EMIBF$_4$:aPEO	12 - 12.5	0.38
1:3 EMIBPh$_4$:aPEO	> 300	2.2×10^{-3}
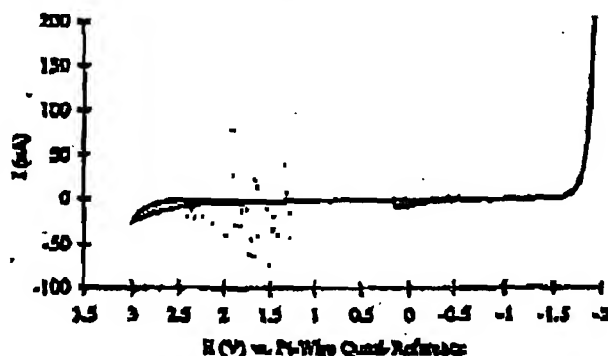
Figure 2. Staircase cyclic voltammogram at 33 µm GC for 1:1 aPEO:EMIPF$_6$ gel.

Acknowledgment

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